Effect of Ce addition on catalytic activity of Cu-Mn catalysts for Water Gas Shift (WGS) reaction

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WGS ($CO+H_2O \leftrightarrows H_2+CO_2$) reaction is well known and matured technology to react carbon monoxide with water producing carbon dioxide and hydrogen. Generally, this reaction takes place in series of two reaction steps due to the limitations in thermodynamic equilibrium and kinetics. The first one is called as LTS (Low Temperature shift) and the other is HTS (High Temperature shift). In LTS, Cu-based catalysts have been studied with a variety of support materials to achieve stable catalytic structure and high catalytic activity.

Especially, Cu-Mn catalyst have been reported to improve the WGS reaction activity because Cu-Mn spinel phase formed lead the dispersion of Cu ion [1-3]. Recently, introduction of transition metal or lanthanide based metal into Cu/Mn catalysts have been attempted by various researchers to improve the catalytic activity and stability. Oxygen storage capacity (OSC) of the lanthanide metal oxides are mainly attributed to the improved activity. It has been reported that Ce doping provides OSC and oxygen vacancy to the catalyst and it helps OH groups to be associatively adsorbed on catalyst surface and facilitate the WGS reaction. Small amount of Ce addition in Cu-Mn spinel oxide might tune the characteristics of Cu-Mn catalyst without severe change of chemical composition.

In this study, Cu/Mn/Ce catalysts for water gas shift (WGS) reaction were synthesized by urea-nitrate combustion method with the fixed molar ratio of Cu/Mn as 1:4 and 1:1 with the doping concentration of Ce from 0.3 to 0.8 mol%. The prepared catalysts were characterized with SEM, BET, XRD, XPS, H_2-TPR, CO_2 TPD, N_2O chemisorption analysis. The catalytic activity tests were carried out at a GHSV of 28,000 h^{-1} and a temperature range of 200 to 400 ºC. The Cu-Mn(CM) catalysts formed CM mixed oxide of spinel structure ($Cu_{1.5}Mn_{1.5}O_4$) and manganese oxides (MnO_x). However, when a small amount of Ce was doped, the growth of $Cu_{1.5}Mn_{1.5}O_4$ was inhibited and the degree of Cu dispersion were increased. Also, the doping of Ce on the CM catalyst reduced the reduction temperature and the base site to induce the active site of the catalyst to be exposed on the catalyst surface. From the XPS analysis, it was confirmed that the oxidation state of Cu due to the redox properties of Ce was main factor in the WGS reaction. Consequently, Ce as support and dopant in the water gas shift reaction catalysts exhibited the enhanced catalytic activities on CM catalysts.

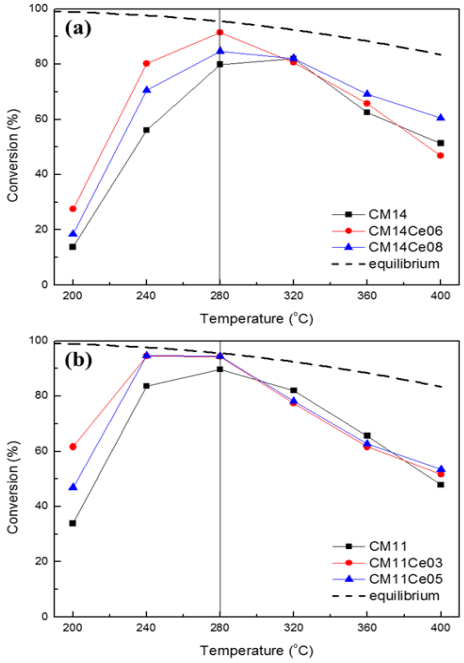

Fig. 1 CO conversion of CM catalysts

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